D E C L A R A T I O N

I, SHINICHI USUI, a Japanese Patent Attorney registered No. 9694, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the Japanese Patent Application Laid-Open No. 7-90591.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 7th day of September, 2000

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[TITLE OF THE INVENTION]

MICROWAVE PLASMA CVD APPARATUS AND METHOD OF FORMING DEPOSITED FILM

[ABSTRACT]

[Object] To dissolve the problem that deposition of a thin film on a wall between a microwave waveguide and a plasma generating chamber causes absorption of microwaves by the thin film and requires frequent maintenance of the apparatus and to enable high speed film deposition

[Constitution] A microwave waveguide 103 conventionally kept at atmospheric pressure is evacuated through a plasma generating chamber 101 and slots 107, and a wall between the microwave waveguide and the plasma generating chamber is omitted. Further, a plasma generating gas introducing opening 108 is moved to the microwave waveguide. Consequently, the pressure inside the microwave waveguide becomes larger than that inside the plasma generating chamber, so that a plasma is generated only in the plasma generating chamber.

[Effect] A wall between the microwave waveguide and the plasma generating chamber becomes dispensable and the maintenance cycle of the apparatus becomes 10 or more times that of the prior art apparatuses.

[CLAIMS]

[Claim 1] A microwave plasma CVD apparatus in which a plasma generating chamber is pressure-reduced by an evacuation means, and a microwave energy is supplied into the plasma generating chamber through a microwave waveguide connected to the plasma generating chamber, thus forming a deposited film on a substrate arranged in the plasma generating chamber or a film forming chamber communicating with the plasma generating chamber, wherein the waveguide has a plurality of slots formed in a plasma generating chamber side surface thereof such that a gas for generating the plasma is introduced into the plasma generating chamber through the slots.

[Claim 2] The plasma CVD apparatus according to claim 1, wherein the configuration of the slot is rectangle such that the short side is 0.5 mm - 3 mm and the long side is 40 mm - 60 mm.

[Claim 3] The plasma CVD apparatus according to claim 2, wherein the interval of the slots is controlled to be 1/4 of the guide wavelength of the microwave energy or an integral multiple thereof.

[Claim 4] The microwave plasma CVD apparatus according to claim 1 to 3, wherein the plasma generating chamber is substantially cylindrical, and the waveguide surrounds the periphery of the plasma generating chamber and is substantially cylindrical.

[Claim 5] The microwave plasma CVD apparatus according to claim 1 to 3, wherein the plasma generating chamber is substantially cylindrical, and the waveguide faces a circular flat plane portion of the plasma generating chamber and is substantially in the shape of a disk.

[Claim 6] The microwave plasma CVD apparatus according to claim 1 to 4, comprising means for generating in the plasma generating chamber a magnetic field which is perpendicular to the electric field of the microwave and

has a flux density about 3.57 x 10^{-11} times (T/Hz) the frequency of the microwave.

[Claim 7] The microwave plasma CVD apparatus according to claim 1 to 6, wherein a substrate support is arranged at a position distant from the plasma.

[Claim 8] The microwave plasma CVD apparatus according to claim 1 to 7, comprising means for irradiating a surface of the film forming substrate with a visible or ultraviolet light.

[Claim 9] The microwave plasma CVD apparatus according to claim 1 to 8, comprising means for applying an rf bias to the substrate support.

[Claim 10] A microwave plasma CVD apparatus in which a plasma generating chamber is pressure-reduced by an evacuation means, a microwave energy is supplied into the plasma generating chamber through a microwave waveguide connected to the plasma generating chamber, a plasma is generated in the plasma generating chamber, thus forming a deposited film on a substrate arranged in the plasma generating chamber or a film forming chamber communicating with the plasma generating chamber, wherein the microwave waveguide is pressure-reducible by the evacuation means such that a pressure differential is formed between the plasma generating chamber and the microwave waveguide.

[Claim 11] The microwave plasma CVD apparatus according to claim 10, wherein the plasma generating chamber is substantially cylindrical, and the waveguide surrounds the periphery of the plasma generating chamber and is substantially cylindrical.

[Claim 12] The microwave plasma CVD apparatus according to claim 10, wherein the plasma generating chamber is substantially cylindrical, and the waveguide faces a circular flat plane portion of the plasma generating chamber and is substantially in the shape of a disk.

[Claim 13] The microwave plasma CVD apparatus according

to claim 10 to 11 comprising means for generating in the plasma generating chamber a magnetic field which is perpendicular to the electric field of the microwave and has a flux density about 3.57 x 10^{-11} times (T/Hz) the frequency of the microwave.

[Claim 14] The microwave plasma CVD apparatus according to claim 10 to 13, wherein a substrate support is arranged at a position distant from the plasma.

[Claim 15] The microwave plasma CVD apparatus according to claim 10 to 14, comprising means for irradiating a surface of the film forming substrate with a visible or ultraviolet light.

[Claim 16] The microwave plasma CVD apparatus according to claim 10 to 15, comprising means for applying an rf bias to the substrate support.

[Claim 17] A deposited film forming method comprising pressure-reducing a plasma generating chamber by an evacuation means; supplying a microwave energy into the plasma generating chamber through a microwave waveguide connected to the plasma generating chamber, generating a plasma in the plasma generating chamber, thus forming a deposited film on a substrate arranged in the plasma generating chamber or a film forming chamber communicating with the plasma generating chamber, wherein the microwave waveguide is pressure-reduced by the evacuation means and the formation of deposited film is carried out while supplying a gas for plasma generation into the plasma generating chamber through the microwave waveguide.

[Claim 18] The deposited film forming method according to claim 17, wherein the pressure inside the plasma generating chamber is made lower than the pressure inside the microwave waveguide.

[Claim 19] The deposited film forming method according to claim 18, wherein the pressure inside the plasma generating chamber is controlled within the range of 0.5

mTorr to 0.5 Torr.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Field of the Invention]

This invention relates to a plasma CVD apparatus using a microwave energy and a deposited film forming method using a microwave energy.

[0002]

[Description of the Prior Art]

Film formation which uses a microwave plasma CVD apparatus is performed, for example, as follows. That is, a gas is introduced into a film forming chamber of the microwave plasma CVD apparatus simultaneously with application of a microwave energy to generate a plasma in the film forming chamber, thus exciting and decomposing the gas to form a deposited film on a substrate arranged in the film forming chamber.

[0003]

With the microwave plasma CVD apparatus, using microwave energy as a source of excitation of a gas can accelerate electrons by an electric field with a higher frequency than that of the RF energy to ionize and excite gas molecules continuously. Therefore, the excitation efficiency and decomposition efficiency of the gas is high, and there is an advantage that a high-density plasma can easily be formed and that film formation can be performed at high speed.

[0004]

The inventor proposed a microwave plasma CVD apparatus using an annular waveguide in which a plurality of slots were formed in the inside surface thereof as a unique, efficient introducing device of microwaves (Patent Application No. H 3-293010). The microwave plasma CVD apparatus is shown in Fig. 9. In Fig. 9, reference

numeral 1101 designates a plasma generating chamber; 1102 a quartz tube which forms the plasma generating chamber 1101; 1103 a slotted annular waveguide for introducing microwaves into the plasma generating chamber 1101; 1104 a microwave introducing section which introduces microwaves 1103 into the annular waveguide 1104. Reference numeral 1106 designates a distribution block for distributing microwaves into two; 1107 a plurality of slots formed at the inner side of the annular waveguide; 1108 an introducing means for a plasma generating gas; 1111 a film forming chamber connected to the plasma generating chamber; 1112 a film forming substrate; 1113 a support for the film forming substrate; 1114 a heater for heating the substrate 1112; 1115 an introducing means for a film forming gas; and 1116 evacuation. The plasma generation and film formation are performed as follows. Evacuation of the inside of the plasma generating chamber 1101 and the film forming chamber 1111 is carried out through an evacuation system (not shown). Then, a plasma generating gas is introduced into the plasma generating chamber 1101 at a predetermined flow rate through the gas introduction opening 1108. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 1101 at a predetermined pressure. A desired power is supplied into the plasma generating chamber 1101 through the annular waveguide 1103 from a microwave power source (not shown). Electrons are accelerated by the microwave electric field by carrying out like this, and a high-density plasma is generated in the plasma generating chamber 1101. If a film forming gas is introduced into the film forming chamber 1111 through the film forming gas introducing pipe 1115 at this time, the film forming gas will be excited by the generated high-density plasma to form a film on a surface of the film forming substrate

1112 laid on the support 1113. In this case, according to the intended use, the film forming gas may be introduced into the introduction opening 1108 for the plasma generating gas.

[0005]

[Problem to be Solved by the Invention]

However, with the apparatus shown in Fig. 9, it is necessary to maintain a pressure differential between the plasma generating chamber as a vacuum tank and the microwave introducing pipe at atmospheric pressure and to prepare a wall for microwave transmission, i.e., the quartz tube 1102. At this time, depending the material for film formation on the substrate, a thin film is deposited on the inner wall of the quartz tube. In such a case, microwaves are absorbed by the thin film, which poses the problem that microwaves can not efficiently introduced into the plasma generating chamber. Such a phenomenon is especially occurred notably when forming a conductive film because the conductive film does not transmit microwaves.

[0006]

[Means for Solving the Problem and its Action]

This invention has been made as a result of extensive study to solve the problem of the conventional microwave plasma CVD apparatus. In the prior art the inside of the microwave waveguide has been kept at atmospheric pressure, while this invention has made it possible to also reduce the pressure inside the microwave waveguide through the slots provided in the microwave waveguide by means of the pressure reducing means of the plasma generating chamber. The quartz tube 1102 of the apparatus shown in Fig. 9 becomes dispensable by such configuration, and even if a deposited film is grown on the film forming substrate 1112, there are no cases where a thin film is deposited on the inside wall of the quartz tube, and microwaves are

absorbed by the deposit, thus preventing introduction of microwaves into the plasma generating chamber.

[0007]

Moreover, the inventor has found that connecting a plasma generating gas introducing means to a microwave waveguide, and reducing the pressure inside the microwave waveguide through slots provided in the microwave waveguide by a pressure-reducing means connected to the plasma generating chamber such that the pressure inside the microwave waveguide is larger than the pressure inside the plasma generating chamber, a plasma becomes difficult to be generated in the microwave waveguide, so that a plasma can effectively be formed in the plasma generating chamber.

[0008]

This invention has been made based on the finding. A first embodiment of the microwave plasma CVD apparatus of the invention is as follows. Namely, it is a microwave plasma CVD apparatus in which a plasma generating chamber is pressure-reduced by an evacuation means, and a microwave energy is supplied into the plasma generating chamber through a microwave waveguide connected to the plasma generating chamber, thus forming a deposited film on a substrate arranged in the plasma generating chamber or a film forming chamber communicating with the plasma generating chamber, wherein the waveguide has a plurality of slots formed in a plasma generating chamber side surface thereof such that a gas for generating the plasma is introduced into the plasma generating chamber through the slots

[0009]

A second embodiment of the microwave plasma CVD apparatus of the invention is follows. Namely, it is a microwave plasma CVD apparatus in which a plasma generating chamber is pressure-reduced by an evacuation means, a microwave energy is supplied into the plasma generating chamber

through a microwave waveguide connected to the plasma generating chamber, a plasma is generated in the plasma generating chamber, thus forming a deposited film on a substrate arranged in the plasma generating chamber or a film forming chamber communicating with the plasma generating chamber, wherein the microwave waveguide is pressure-reducible by the evacuation means such that a pressure differential is formed between the plasma generating chamber and the microwave waveguide.

[0010]

The invention also includes a deposited film forming method. The deposited film forming method of the invention comprises pressure-reducing a plasma generating chamber by an evacuation means; supplying a microwave energy into the plasma generating chamber through a microwave waveguide connected to the plasma generating chamber, generating a plasma in the plasma generating chamber, thus forming a deposited film on a substrate arranged in the plasma generating chamber or a film forming chamber communicating with the plasma generating chamber, wherein the microwave waveguide is pressure-reduced by the evacuation means and the formation of deposited film is carried out while supplying a plasma generating gas into the plasma generating chamber through the microwave waveguide.

[0011]

According to the invention, the above described technical problem is solved and efficient formation of a deposited film is attained.

[0012]

That is, according to the invention, the problem that the quartz tube which constitutes the inside wall of the plasma generating chamber a microwave CVD apparatus is necessary, and that the introduction of microwaves into the plasma generating chamber is prevented by a thin film

deposited on the wall of the quartz tube is solved. Therefore, the maintenance cycle of the apparatus becomes long and the reliability and operating efficiency of the apparatus is improved. Furthermore, according to the invention, efficient generation of a plasma is attained, and it is possible to form a high-quality deposited film efficiently.

[0013]

In the invention, it is preferable that the pressure inside the plasma generating chamber is kept at 0.5 torr or less, and that the pressure inside the microwave waveguide is kept at 1.0 torr or more.

[0014]

Since it is difficult to from a plasma at a pressure of 1 Torr or more, the above is effective in generating a plasma only in the plasma generating chamber. For this reason, if the instant system is used, microwaves can be uniformly and efficiently introduced into the plasma generating chamber, and a uniform and high-density plasma can be generated.

[0015]

An example of the apparatus is shown in Fig. 1. Formation of a deposited film using the apparatus shown in Fig. 1 comprises pressure-reducing a microwave waveguide 103 by an evacuation means 116, and supplying a plasma generating gas through a microwave waveguide 103 to a plasma generating chamber 101 to form a deposited film. Moreover, the apparatus is a microwave plasma CVD apparatus in which the microwave waveguide 103 is pressure-reducible by the evacuation means 116 and a pressure differential is formed between the plasma generating chamber 101 and the microwave waveguide 103. Further, the waveguide of the apparatus has a plurality of slots formed in a plasma generating chamber side surface thereof such that a gas for generating the plasma is

introduced into the plasma generating chamber through the slots.

[0016]

The plasma generation and film formation using this system are performed as follows. Evacuation of the inside of the plasma generating chamber 101 and the film forming chamber 111 is carried out through an evacuation system (not shown). Then, a plasma generating gas is introduced into the plasma generating chamber 101 at a predetermined flow rate through the waveguide 103 and the slots 107 from the gas introduction opening 108. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 101 and the film forming chamber 111 at a predetermined pressure. A desired power is supplied into the plasma generating chamber 101 through the waveguide 103 from a microwave power source (not shown) to generate a plasma in the plasma generating chamber 101. If a film forming gas is introduced into the film forming chamber 111 through the film forming gas introducing pipe 115 at this time, the film forming gas will be excited by the generated high-density plasma to form a deposited film on a surface of the film forming substrate 112 laid on the support 113. In this case, according to the intended use, the film forming gas may be introduced into the introduction opening 108 for the plasma generating gas.

[0017]

When using the microwave introducing device of the invention, the frequency of the microwave used can be suitably chosen within the range of 0.8 GHz to 20 GHz including 2.45 GHz.

[0018]

The configuration of the waveguide used in the invention may be either a cylinder or other shapes such as a disk, a polygon, or the like. As to the configuration of the

cross section of the waveguide, it may be either a rectangle with the same dimension as WRT-2 standard waveguide or other shapes such as a circle, semicircle with any dimension, as long as microwaves can propagate therethrough. As the material of the annular waveguide, it is possible to use double layer plated stainless steel with a copper coating and an additional silver coating; metals such as Cu, Al, Fe, Ni or alloys; insulators such as various glass, quartz, silicon nitride, alumina, acrylic resin, polycarbonate, polyvinyl chloride, and polyimide coated with a metal thin film such as of Al, W, Mo, Ti, Ta, Cu, and Ag, as long as it has a sufficient mechanical strength and the surface is covered with an electrically conductive layer of a thickness larger than the permeation depth of the microwave.

[0019]

The configuration of the slots provided in the microwave plasma CVD apparatus of the invention includes a rectangle with a long side perpendicular to, parallel to or obliquely crossing the travelling direction of microwaves, a circle, a polygon, an iron array-like shape, a star-like shape, as long as it can introduce microwaves therethrough and has such a conductance as to attain a high inner pressure of the waveguide such that no discharge is generated in the waveguide. However, considering the ease of efficient introduction or adjustment of the rate of leakage, a rectangular shape of 40 mm to 60 mm x 0.5 mm to 3 mm with the long side perpendicular to the travelling direction of microwaves is the optimum. The length of slots is adjusted such that the amount of leakages of microwaves through each slot may become almost equal. The adjustment of the length of slots may be made by sticking a conductive tape or using a shutter. The interval between the slots to be provided may be either 1/4 of the guide wavelength or an integral multiple thereof, and the

slots need not be provided at a portion not requiring plasma generation.

[0020]

Although the microwave CVD apparatus of the invention hardly effects discharge in the waveguide but effects discharge only after microwaves have been introduced into the plasma generating chamber, it is also possible depending on the intended use to effect discharge resonantly inside the waveguide and to supply a high-density nonionic active species from a portion of strong discharge. In this case, a configuration of the slot can be adopted which attains an inner pressure of the waveguide within such a range as to effect discharge in the waveguide, and a rectangular shape of 40 mm to 60 mm x 2 mm to 5 mm with the long side perpendicular to the travelling direction of microwaves is the optimum.

[0021]

Moreover, a magnetic field generating means may be further provided to higher the density of plasma. As a magnetic field generating means, a permanent magnet as well as a coil can be used as long as a magnetic field perpendicular to the electric field in the vicinity of a slot of the waveguide can be generated. Moreover, the magnetic circuit that can be used includes not only a mirror magnetic field but also a divergent magnetic field, a multi-cusp magnetic field, or a cylinder magnetron magnetic field. When using a coil, a cooling means such as a water-cooling mechanism or air cooling mechanism may be used to prevent overheating.

[0022]

By using the above microwave plasma CVD apparatus, a deposited film of good quality can be formed uniformly and efficiently on a film forming substrate arranged in the plasma generating chamber or the film forming chamber connected to the plasma generating chamber.

[0023]
Moreover, since microwaves can be introduced into the plasma generating chamber by using the above microwave plasma CVD apparatus without passing through a quartz tube, there is no case where a film which absorbs microwaves is formed on a quartz tube, so that microwave becomes difficult to be introduced into the plasma generating chamber. Thus, the maintenance cycle becomes long, and the reliability and operating efficiency of the apparatus improves.
[0024]
[Examples of plasma CVD apparatus]
Although examples of the apparatus are given below to explain the microwave plasma CVD apparatus of the invention more concretely, it is to be understood that the invention is not limited to the example of the apparatus.
[0025] System Example 1
A microwave plasma CVD apparatus using an annular waveguide which is an example of the invention is shown in Fig. 1 (A), and its microwave introducing device is shown in Fig. 1 (B). Reference numeral 101 designates a plasma generating chamber; 103 a slotted annular waveguide for introducing microwaves into the plasma generating chamber 101; 104 a microwave introducing section for introducing microwaves 1103 into the annular waveguide 103; 105 a microwave introducing window provided at the introducing section. Reference numeral 106 designates a distribution block for distributing microwaves into two; 107 a plurality of slots formed at the inner side of the annular waveguide; 108 an introducing means for a plasma generating gas; 111 a film forming chamber connected to the plasma generating chamber; 112 a film forming substrate; 113 a support for the film forming substrate; 114 a heater for heating the substrate 112; 115 an introducing means for a film forming gas; and 116 an

evacuation system.

[0026]

The annular waveguide 103 has the same dimension of the inside wall cross section 27 mm x 96 mm as the WRT-2 standard waveguide, and the central diameter is 354 mm. The material of the annular waveguide 103 is stainless steel to maintain the mechanical strength, and in order to suppress the propagation loss of microwaves, the inside wall surface is subjected to bilayer plating of a coating of copper and a coating of silver further provided thereon.

[0027]

The configuration of the slots 107 is a rectangle with a length of 42 mm and a width of 2 mm, and the slots are formed at a interval of 1/4 of the guide wavelength. Although it is dependent on the frequency of microwaves and the dimension of the cross section of the waveguide used, the guide wavelength is about 159 mm when the waveguide of the above dimension and microwaves with a frequency of 2.45 GHz are used. In the annular waveguide 103 used here, 28 slots are formed at an interval of about 40 mm.

[0028]

A 4 stub tuner, a directional coupler, an isolator and a microwave power source with a frequency of 2.45 GHz are connected to the microwave introducing section 104 in the mentioned order.

[0029]

The plasma generation and film formation using this system are performed as follows. Evacuation of the inside of the plasma generating chamber 101 and the film forming chamber 111 is carried out through an evacuation system (not shown). Then, a plasma generating gas is introduced into the plasma generating chamber 101 at a predetermined flow rate through the waveguide 103 and the slots 107 from the

gas introduction opening 108. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 101 and the film forming chamber 111 at a predetermined pressure. A desired power is supplied into the plasma generating chamber 101 through the waveguide 103 from a microwave power source (not shown) to generate a plasma in the plasma generating chamber 101. If a film forming gas is introduced into the film forming chamber 111 through the film forming gas introducing pipe 115 at this time, the film forming gas will be excited by the generated high-density plasma to form a film on a surface of the film forming substrate 112 laid on the support 113. In this case, according to the intended use, a gas for film formation may be introduced into the introduction opening 108 for a plasma generating gas.

[0030]

Using the microwave plasma CVD apparatus shown in Fig. 1 (A), a plasma was generated under the conditions of a N_2 flow rate 500 sccm, a pressure 5 mTorr, and a microwave power 1 kW, and the uniformity of the electron density of the generated plasma was evaluated. The evaluation of uniformity of the electron density was performed as follows by the probe method. The voltage applied to the probe was changed within the range of -50 to +50 V, the current which flows through the probe was measured with an I-V measuring instrument, and the electron density was calculated by the Langmuir's method from the obtained I-V curve. The electron density was measured at 19 points within a central cross section of the plasma generating chamber, and the dispersion in its (maximum value)/(minimum value) was determined to evaluate the uniformity. Consequently, the electron density was 9.6 x $10^{11}/cm^3$ ± 4.8 % within a ϕ200 plane, and it was confirmed that a high-density and uniform plasma was formed.

[0031] System Example 2

A microwave plasma CVD apparatus using a disk-like waveguide which is an example of the invention is shown in Figs. 2 (A) and 2 (B). Reference numeral 201 designates a plasma generating chamber; 203 a slotted disk-like waveguide for introducing microwaves into the plasma generating chamber 201; 204 a microwave introducing section for introducing microwaves into the disk-like waveguide 203; 205 a microwave introducing window provided at the introducing section. Reference numeral 206 designates a distribution block for distributing microwaves into two; 207 a plurality of slots formed at the inner side of the disk-like waveguide; 208 an introducing means for a plasma generating gas; 211 a film forming chamber connected to the plasma generating chamber. Reference numeral 212 a film forming substrate; 213 a support for the film forming substrate 212; 214 a heater for heating the substrate; 215 an introducing means for a film forming gas; and 216 an evacuation system. To the microwave introducing section 204 are connected a 4 stub tuner, a directional coupler, an isolator and a microwave power source with a frequency of 2.45 GHz in the mentioned order.

[0032]

The plasma generation and film formation are performed as follows. Evacuation of the inside of the plasma generating chamber 201 and the film forming chamber 211 is carried out through an evacuation system (not shown). Then, a plasma generating gas is introduced into the plasma generating chamber 201 at a predetermined flow rate through the disk-like waveguide 203 and the slots 107 from the gas introduction opening 208. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 201 and the film forming chamber 211 at

a predetermined pressure. A desired power is supplied into the plasma generating chamber 201 through the disk-like waveguide 203 from a microwave power source (not shown) to generate a plasma in the plasma generating chamber 201. If a gas for film formation is introduced into the film forming chamber 211 through the film forming gas introducing pipe 215 at this time, the gas for film formation will be excited by the generated plasma to form a film on the surface of the film forming substrate 212 laid on the support 213. In this case, according to the intended use, a gas for film formation may be introduced into the introduction opening 208 for a plasma generating gas.

[0033]

Using the microwave plasma CVD apparatus shown in Fig. 2 (A), a plasma was generated under the conditions of a N_2 flow rate 500 sccm, a pressure 3 mTorr, and a microwave power 800 W, and the uniformity of the electron density of the generated plasma was evaluated. Consequently, the electron density was $8.4 \times 10^{11}/cm^3 \pm 3.6$ % within a ϕ200 plane, and it was confirmed that a high-density and uniform plasma was formed.

[0034] <u>System Example 3</u>

An example of a microwave plasma CVD apparatus with a magnetic filed is shown in Fig. 3 (A), and its microwave introducing device is shown in Fig. 3 (B). Reference numeral 301 designates a plasma generating chamber; 303 a slotted annular waveguide for introducing microwaves into the plasma generating chamber 301; 304 a microwave introducing section for introducing microwaves into the annular waveguide 303; 305 a microwave introducing window provided at the introducing section 304. Reference numeral 306 designates a distribution block for distributing microwaves into two; 307 a plurality of slots formed at the inner side of the annular waveguide 304; 308

an introducing means for a plasma generating gas. Reference numeral 309 is a coil for generating a magnetic field parallel to the electric filed within the plasma generating chamber; 311 a film forming chamber connected to the plasma generating chamber; 312 a film forming substrate; 313 a support for the film forming substrate; 314 a heater for heating the substrate 312; 315 an introducing means for a film forming gas; and 316 an evacuation system.

[0035]

The plasma generation and film formation are performed as follows. Evacuation of the inside of the plasma generating chamber 301 and the film forming chamber 311 is carried out through an evacuation system (not shown). Then, a plasma generating gas is introduced into the plasma generating chamber 301 at a predetermined flow rate through the annular waveguide 303 and the slots 307 from the gas introduction opening 108. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 301 at a predetermined pressure. Then, after a desired power is supplied to the coil 309 from a D.C. power source (not shown) to generate a uniform magnetic field with a central magnetic flux density 87.5 mT in the plasma generating chamber 301, a desired power is supplied into the plasma generating chamber 301 through the annular waveguide 303 from a microwave power source (not shown). The electrons carrying out screw motion around the magnetic line generated in the plasma generating chamber 301 with the coil 309 absorbs microwaves resonantly to be accelerated, thus forming a high-density plasma in the plasma generating chamber 301. If the gas for film formation is introduced into the film forming chamber 311 through the film forming gas introducing pipe 315 at this time, the film forming gas

will react with the plasma generating gas excited by the generated high-density plasma to form a film on a surface of the film forming substrate 312 laid on the support 313. In this case, according to the intended use, the film forming gas may be introduced into the introduction opening 108 for the plasma generating gas.

[0036] System Example 4

An example of a microwave isolated plasma CVD apparatus is shown in Fig. 4 (A), and its microwave introducing device is shown in Fig. 4 (B). Reference numeral 401 designates a plasma generating chamber; 403 a slotted annular waveguide for introducing microwaves into the plasma generating chamber 401; 404 a microwave introducing section for introducing microwaves into the annular waveguide 403; 405 a microwave introducing window provided at the introducing section 404. Reference numeral 406 designates a distribution block for distributing microwaves into two; 407 a plurality of slots formed at the inner side of the annular waveguide 404; 408 an introducing means for a plasma generating gas; 411 a film forming chamber connected to the plasma generating chamber; 412 a film forming substrate; 413 a support for the substrate 412; 414 a heater for heating the substrate 412; 415 an introducing means for a film forming gas; 416 an evacuation system; 417 a perforated separating plate for separating the plasma generating chamber 401 and the film forming chamber 411.

[0037]

The plasma generation and film formation are performed as follows. Evacuation of the inside of the plasma generating chamber 401 is carried out through an evacuation system (not shown). Then, a plasma generating gas is introduced into the plasma generating chamber 401 at a predetermined flow rate through the annular waveguide 403 and the slots 407 from the gas introduction opening

408. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 401 at a predetermined pressure. A desired power is supplied into the plasma generating chamber 401 through the annular waveguide 403 from a microwave power source (not shown) to form a plasma in the plasma generating chamber 401. If the gas for film formation is introduced into the film forming chamber 411 through the film forming gas introducing pipe 415 at this time, the film forming gas will react with the plasma generating gas excited by the generated plasma to form a film on a surface of the film forming substrate 412 laid on the support 413. In this case, according to the intended use, the film forming gas may be introduced into the introduction opening 408 for the plasma generating gas.

[0038] System Example 5

An example of a photo-assisted microwave plasma CVD apparatus is shown in Fig. 5 (A), and its microwave introducing device is shown in Fig. 5 (B). Reference numeral 501 designates a plasma generating chamber; 503 a slotted annular waveguide for introducing microwaves into the plasma generating chamber 501; 504 a microwave introducing section for introducing microwaves into the annular waveguide 503; 505 a microwave introducing window provided at the introducing section 504. Reference numeral 506 designates a distribution block for distributing microwaves into two; 507 a plurality of slots formed at the inner side of the annular waveguide 504; 508 an introducing means for a plasma generating gas; 511 a film forming chamber connected to the plasma generating chamber. Reference numeral 512 designates a film forming substrate; 513 a support for the substrate 512; 514 a heater for heating the substrate 512; 515 an introducing means for a film forming gas; 516 an evacuation system.

Reference numeral 521 is an illumination system for irradiating a surface of the substrate 512 with a visible or ultraviolet light and 525 is a light introducing window for introducing the visible or ultraviolet light from the illumination system 521 to the film forming chamber 511 through the plasma generating chamber 501. The illumination system 521 consists of the light source 522, a reflecting mirror 523 for condensing the light from the light source 522, and an integrator 524 consisting of a number of convex lenses for making the light uniform.

[0039]

The plasma generation and film formation are performed as follows. Evacuation of the inside of the plasma generating chamber 501 and the film forming chamber 511 is carried out through an evacuation system (not shown). Then, the surface of the substrate 512 is irradiated with a visible or ultraviolet light from the illumination system through the light introducing window with the substrate being maintained at a predetermined temperature. Then, a plasma generating gas is introduced into the plasma generating chamber 501 at a predetermined flow rate through the annular waveguide 503 and the slots 507 from the gas introduction opening 508. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 501 at a predetermined pressure. A desired power is supplied into the plasma generating chamber 501 through the annular waveguide 503 from a microwave power source (not shown) to form a plasma in the plasma generating chamber 501. If the gas for film formation is introduced into the film forming chamber 511 through the film forming gas introducing pipe 515 at this time, the film forming gas will be excited by the generated high-density plasma to form a film on a surface of the film forming substrate 512 laid on the support 513.

At the time, since the surface is irradiated with the visible or the ultraviolet light, higher quality film formation is attained. In this case, according to the intended use, the film forming gas may be introduced into the gas introduction opening 508 for the plasma generating gas.

[0040]

As the light source 522 of the illumination system 521, there can be used any light source having such a wavelength as to be absorbed by a precursor deposited on the substrate surface, such as a low-pressure mercury lamp, a high-pressure mercury lamp, an extra-high pressure mercury lamp, a xenon-mercury lamp, a xenon lamp, a deuterium lamp, Ar resonance-line lamp, Kr resonance-line lamp, Xe resonance-line lamp, an excimer laser, an Ar+ laser with double higher harmonic, N_2 laser, a YAG laser with triple higher harmonic, or the like.

[0041] System Example 6

A biased microwave plasma CVD apparatus is shown in Fig. 6 (A), and its microwave introducing device is shown in Fig. 6 (B). Reference numeral 601 designates a plasma generating chamber; 603 a slotted annular waveguide for introducing microwaves into the plasma generating chamber 601; 604 a microwave introducing section for introducing microwaves into the annular waveguide 603. Reference numeral 605 designates a microwave introducing window provided at the introducing section 604; 606 a distribution block for distributing microwaves into two; 607 a plurality of slots formed at the inner side of the annular waveguide 603;

608 an introducing means for a plasma generating gas; 611 a film forming chamber connected to the plasma generating chamber. Reference numeral 612 a film forming substrate; 613 a support for the substrate 612; 614 a heater for heating the substrate 612; 615 an introducing means for a

film forming gas; 616 an evacuation system. Reference numeral 618 is a high frequency rod for applying a high frequency bias to the support 613, and 619 are insulating rods for insulating the support 613 from grounding potential.

[0042]

The plasma generation and film formation are performed as follows. Evacuation of the inside of the plasma generating chamber 601 and the film forming chamber 611 is carried out through an evacuation system (not shown). Then, a plasma generating gas is introduced into the plasma generating chamber 601 at a predetermined flow rate through the annular waveguide 603 and the slots 607 from the gas introduction opening 608. Next, a conductance valve (not shown) provided in the evacuation system (not shown) is adjusted to keep the inside of the plasma generating chamber 601 and the film forming chamber 611 at a predetermined pressure. Then, after a high frequency has been applied to the support 613 through the high frequency rod 618, a desired power is supplied into the plasma generating chamber 601 through the annular waveguide 603 from a microwave power source (not shown) to form a plasma in the plasma generating chamber 601. If the gas for film formation is introduced into the film forming chamber 611 through the film forming gas introducing pipe 615 at this time, the film forming gas will be excited by the generated plasma, and the ion component is accelerated by a sheath electric field generated on the support surface to form a film on the surface of the film forming substrate 612 laid on the support 613. In this case, according to the intended use, the film forming gas may be introduced into the introduction opening 608 for the plasma generating gas.

[0043] <u>System Example 7</u>

A microwave plasma CVD apparatus provided with an annular

microwave introducing device and a disk-like microwave introducing device in combination is shown in Fig. 7 (A). The disk-like microwave introducing device is shown in Fig. 8 (B), and the annular microwave introducing device is shown in Fig. 8 (C). Reference numeral 701 is a plasma generating chamber; 703a, 703b are slotted waveguides for introducing microwaves into the plasma generating chamber 701 (703a is the annular waveguide and 703b is the disk-like waveguide; hereinafter a and b attached to the reference numerals designate a component of the annular waveguide and a component of the disk-like waveguide, respectively); 704 a microwave introducing section for introducing microwaves into the annular waveguide 703; 705 a microwave introducing window provided at the introducing section 704. Reference numeral 706 a distribution block for distributing microwaves into two; 707 a plurality of slots formed at the inner side of the annular waveguide 703; 708 an introducing means for a plasma generating gas; 711 a film forming chamber connected to the plasma generating chamber. Reference numeral 712 a film forming substrate; 713 a support for the substrate 712; 714 a heater for heating the substrate 712; 715 an introducing means for a film forming gas; 716 an evacuation system.

[0044]

The pressure inside the plasma generating chamber and the film forming chamber of the microwave plasma CVD apparatus of the invention can be preferably selected within the range of 0.5 mTorr to 0.5 Torr.

[0045]

Although the substrate temperature at the time of forming a film by the microwave plasma CVD apparatus of the invention somewhat varies depending on the kind of the gas for film formation to use, the kind of the deposited film, and the intended use, it is generally within the range of 50 to 600°C preferably, and is within the range of 100 to

400°C optimally.

[0046]

The formation of a deposited film by the microwave plasma CVD apparatus of the invention can be used to efficiently form various kinds of deposited films such as an insulating film such as Si_3N_4, SiO_2, Ta_2O_5, TiO_2, TiN, Al_2O_3, AlN, MgF_2, etc., a semiconductor film such as of a-Si, poly-Si, SiC, GaAs, etc. and a metal film such as of Al, W, Mo, Ti, Ta, by suitably selecting a gas to use.

[0047]

Moreover, the microwave plasma CVD apparatus of the invention is applicable also to surface modification. For example, by suitably selecting a gas to use, the apparatus can be applied to oxidation, nitridation or doping with B, As, P, etc. of a substrate or surface layer such as of Si, Al, Ti, Zn, Ta, etc. Furthermore, the film formation technique adopted in the invention is applicable also to a cleaning method. In this case, it can also be used for cleaning of an oxide, organic substance, heavy metal, etc.

[0048]

The substrate on which a film is to be formed by the plasma CVD apparatus of the invention may be either semiconductive, conductive, or insulating. Moreover, these substrates may be applied with a D.C. bias of -500 V to +200 V or an alternating bias of a frequency of 40 Hz to 300 MHz for improving performances such as denseness, adhesion, and step coverage.

[0049]

As a conductive substrate, there can be included a metal such as Fe, Ni, Cr, Al, Mo, Au, Nb, Ta, V, Ti, Pt, Pb, etc. or an alloy thereof such as brass, stainless steel, etc.

[0050]

As an insulating substrate, there can be included a film or sheet of SiO_2-based quartz or various kinds of glass,

inorganic substance such as Si_3N_4, NaCl, KCl, LiF, CaF_2, BaF_2, Al_2O_3, AlN, MgO, etc., organic substance such as polyethylene, polyester, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, polyvinylidene chloride, polystyrene, polyamide, and polyimide, etc.

[0051]

As a gas for deposited film formation, generally known gases can be used.

[0052]

As for a gas which can be easily decomposed by the action of a plasma to be deposited singularly, it is desirable to introduce it to the film forming chamber through a film forming gas introducing means provided in the film forming chamber or the like for achievement of a stoichiometric composition or for prevention of film deposition in the plasma generating chamber. Moreover, as for a gas which is difficult to be easily decomposed by the action of a plasma to be deposited singularly, it is desirable to introduce it to the plasma generating chamber through a plasma generating gas introducing means provided in the plasma generating chamber or the like.

[0053]

As the Si atom-containing material introduced through the film forming gas introducing means in the case of forming a thin film of an Si-based semiconductor such as a-Si, poly-Si, or SiC, there can be included those which are in a gaseous state at ordinary temperature and pressure or which are gassified easily, for example, inorganic silanes such as SiH_4 or Si_2H_6; organic silanes such as tetraethylsilane (TES), tetramethylsilane (TMS), dimethylsilane (DMS); or halosilanes such as SiF_4, Si_2F_6, $SiHF_3$, SiH_2F_2, $SiCl_4$, Si_2Cl_6, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, or $SiCl_2F_2$. In addition, as a plasma generating gas introduced through the plasma generating gas introducing opening in this case, there may be included H_2, He, Ne, Ar,

Kr, Xe, and Rn.

[0054]

As the Si atom-containing material introduced through the film forming gas introducing means in the case of forming a thin film based on an Si compound such as Si_3N_4 or SiO_2, the following materials that maintain a gaseous state at ordinary temperature and pressure or that are gassified easily: inorganic silanes such as SiH_4 or Si_2H_6; organic silanes such as tetraetoxysilane (TEOS), tetrametoxysilane (TMOS), octamethylcyclotetrasilane (OMCTS); or halosilanes such as SiF_4, Si_2F_6, $SiHF_3$, SiH_2F_2, $SiCl_4$, Si_2Cl_6, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, or $SiCl_2F_2$. In addition, as a starting material introduced through the plasma generating gas introducing opening in this case, there can be included N_2, NH_3, N_2H_4, hexamethyldisilazane (HMDS), O_2, O_3, H_2O, NO, N_2O, NO_2, and so on.

[0055]

As the metal atom-containing material introduced through the film forming gas introducing means in the case of forming a thin metal film such as of Al, W, Mo, Ti, or Ta includes organic metals such as trimethyl aluminium (TMAl), triethyl aluminium (TEAl), triisobutyl aluminium (TIBAl), dimethyl aluminium hydride (DMAlH), tungsten carbonyl ($W(CO)_6$), molybdenum carbonyl ($Mo(CO)_6$), trimethyl gallium (TMGa), and triethyl gallium (TEGa); and halogenated metals such as $AlCl_3$, WF_6, $TiCl_3$, and $TaCl_5$. In addition, as a plasma generating gas introduced through the plasma generating gas introducing opening in this case, there may be included H_2, He, Ne, Ar, Kr, Xe, Rn.

[0056]

As the metal atom-containing material introduced through the film forming gas introducing means in the case of forming a thin metal compound film such as of Al_2O_3, AlN, Ta_2O_5, TiO_2, TiN, or WO_3 includes organic metals such as trimethyl aluminium (TMAl), triethyl aluminium (TEAl),

triisobutyl aluminium (TIBAl), dimethyl aluminium hydride (DMAlH), tungsten carbonyl ($W(CO)_6$), molybdenum carbonyl ($Mo(CO)_6$), trimethyl gallium (TMGa), and triethyl gallium (TEGa); and halogenated metals such as $AlCl_3$, WF_6, $TiCl_3$, and $TaCl_5$. In addition, as a starting gas introduced through the plasma generating gas introducing opening in this case, there can be included O_2, O_3, H_2O, NO, N_2O, NO_2, N_2, NH_3, N_2H_4, hexamethyldisilazane (HMDS), and so on.

[0057]

As the oxidizing gas introduced through the plasma generating gas introducing opening in the case of oxidizing a surface of the substrate to form a film, there may be included O_2, O_3, H_2O, NO, N_2O, NO_2, or the like. In addition, as the nitriding gas introduced through the plasma generating gas introducing opening in the case of nitriding a surface of the substrate to form a film, there may be included N_2, NH_3, N_2H_4, hexamethyldisilazane (HMDS), and so on. In this case, since a film is not deposited, no starting gas is introduced through the film forming gas introducing opening, or the same gas as a gas introduced through the plasma generating gas introducing opening is introduced through the film forming gas introducing means.

[0058]

As the cleaning gas introduced through the plasma generating gas introducing opening in the case of cleaning an organic matter on the substrate surface, there may be included O_2, O_3, H_2O, NO, N_2O, NO_2, and so on. Further, as the cleaning gas introduced through the plasma generating gas introducing opening in the case of cleaning an inorganic matter on the substrate surface, there may be included F_2, CF_4, CH_2F_2, C_2F_6, CF_2Cl_2, SF_6, NF_3, or the like. In this case, since a film is not deposited, no starting gas is introduced through the film forming gas introducing opening, or the same gas as a gas introduced through the plasma generating gas introducing opening is introduced

through the film forming gas introducing means.

[0059]

[Examples]

The present invention is specifically described below with reference to examples, but this invention is not limited to these examples.

[0060] Example 1

Using the microwave plasma CVD apparatus shown in Fig. 1 (A), a silicon nitride film for a magneto-optical disc was formed.

[0061]

A polycarbonate (PC) substrate (ϕ 3.5 inches) was used as the substrate 112. First, after placing the PC substrate 112 on the substrate support 113, evacuation of the inside of the plasma generating chamber 101 and the film forming chamber 111 was carried out through an evacuation system (not shown) to reduce the inside pressure to 10^{-6} Torr. Nitrogen gas at a flow rate of 200 sccm was introduced into the plasma generating chamber 101 via the plasma generating gas introducing opening 108. At the same time, monosilane gas at a flow rate of 200 sccm was introduced into the film forming chamber 111 via the film forming gas introducing means 115. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the film forming chamber 111 at 20 mTorr. A microwave power source of 2.45 GHz was used to supply a microwave power of 1 kW through the annular waveguide 103 into the plasma generating chamber 101. Thus, a plasma was generated in the plasma generating chamber 101. At this time, the nitrogen gas introduced via the plasma generating gas introducing opening 108 was excited and decomposed in the plasma generating chamber 101 to form an active species, which was then transported toward the silicon substrate 112 to react with the monosilane gas introduced via the film

forming gas introducing means 115, thereby forming a silicon nitride film in 100 nm thickness on the silicon substrate 112. After the film was formed, the film formation speed and the film quality such as refractive index were evaluated.

[0062]

The film formation speed of the silicon nitride film obtained was very large, 850 nm/min, and with respect to the film quality, the refractive index was 2.2 and the stress was 1.8×10^9 dyne/cm^2, and the film was therefore confirmed to be very excellent. Further, although the formed film was rich in silicon with an Si/N ratio of 3.1 and had a high conductivity, films with stable thickness and quality were obtained up to 10,000 times film formation which was the maintenance cycle determined by particle generation.

[0063] Comparative Example 1

A silicon nitride film was formed by following the same procedure as Example 1 except that the apparatus shown in Fig. 9 was used instead of the apparatus shown in Fig. 1.

[0064]

In the apparatus of Fig. 1 used in Example 1, the microwave waveguide 103 and the plasma generating chamber 101 are not separated by a quartz tube, while in the apparatus of Fig. 9 used in the present comparative example the both are separated by the quartz tube 1102.

[0065]

In the present comparative example, film formation was carried out following the same procedure as Example 1 except that nitrogen gas was introduced through the plasma generating gas introducing opening 1108, and monosilane gas was introduced through the film forming gas introducing pipe 1115.

[0066]

As a result, in the present comparative example,

maintenance had to be carried out to remove a deposit on the quartz tube after about 1000 times deposited film formation.

[0067] Example 2

The microwave plasma CVD apparatus shown in Fig. 2 was used to form a silicon nitride film serving to protect a semiconductor element.

[0068]

A p-type single crystal silicon substrate (face orientation [100]; resistivity: 10 Ωcm) was used as the substrate 212. First, after placing the silicon substrate 212 on the substrate support 213, evacuation of the inside of the plasma generating chamber 201 and the film forming chamber 211 was carried out through an evacuation system (not shown) to reduce the inside pressure to 10^{-6} Torr. Then, a heater (not shown) was energized to heat the silicon substrate 212 to 300°C and maintained the substrate at that temperature. Nitrogen gas at a flow rate of 500 sccm was introduced into the plasma generating chamber 201 via the plasma generating gas introducing opening 208. At the same time, monosilane gas at a flow rate of 100 sccm was introduced into the film forming chamber 211 via the film forming gas introducing means 215. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the film forming chamber 211 at 30 mTorr. A microwave power source of 2.45 GHz was used to supply a microwave power of 500 W through the disk-like waveguide 203 into the plasma generating chamber 201. Thus, a plasma was generated in the plasma generating chamber 201. At this time, the nitrogen gas introduced via the plasma generating gas introducing opening 208 was excited and decomposed in the plasma generating chamber 201 to form an active species, which was then transported toward the silicon substrate 212 to react with the monosilane gas

introduced via the film forming gas introducing means 215, thereby forming a silicon nitride film in 1.0 μm thickness on the silicon substrate 212. After the film was formed, the film formation speed and the film quality such as stress were evaluated. For the stress, the change in the amount of the warpage of the substrate was measured before and after the film formation using a laser interferometer Zygo (trade name).

[0069]

The film formation speed of the silicon nitride film obtained was very large, 460 nm/min, and with respect to the film quality, the stress was 1.1×10^9 dyne/cm^2, the leak current was 1.2×10^{-10}A/cm^2, and the dielectric strength was 9 MV/cm, and the film was therefore confirmed to be very excellent. Further, films with stable thickness and quality were obtained up to 1000 times film formation which was the maintenance cycle determined by particle generation.

[0070] Example 3

The microwave plasma CVD apparatus shown in Fig. 3 (A) was used to form an i layer of a pin junction type photovoltaic layer for a solar cell. As the substrate 312, a belt-like substrate of SUS 430BA coated with an Al layer as a lower electrode was used.

[0071]

First, after placing the substrate on the substrate support 313, evacuation of the inside of the plasma generating chamber 301 and the film forming chamber 311 was carried out through an evacuation system (not shown) to reduce the inside pressure to 10^{-6} Torr. Then, a heater (not shown) was energized to heat the substrate 312 to 300°C and maintained the substrate at that temperature. Hydrogen gas at a flow rate of 100 sccm was introduced into the plasma generating chamber 311 via the plasma generating gas introducing opening 308. At the same time,

monosilane gas at a flow rate of 300 sccm and silicon tetrafluoride gas at a flow rate of 10 sccm were introduced into the film forming chamber 311 via the film forming gas introducing means 315. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the plasma generating chamber 301 and the film forming chamber 311 at 10 mTorr. A microwave power source of 2.45 GHz was used to supply a microwave power of 1200 W through the annular waveguide 303 into the plasma generating chamber 301. Thus, a plasma was generated in the plasma generating chamber 301. At this time, the hydrogen gas introduced via the plasma generating gas introducing opening 308 was excited and decomposed in the plasma generating chamber 301 to form an active species, which was then transported toward the substrate 312 to react with the monosilane gas and the silicon tetrafluoride gas introduced via the film forming gas introducing means 315, thereby forming an i-type a-Si:H:F film on the substrate 312. After formation of pin three layers, the film quality such as uniformity and photoelectric conversion efficiency was evaluated. The photoelectric conversion efficiency was evaluated under irradiation with a light having an intensity of 0.1 W/cm^2.

[0072]

The uniformity of the obtained pin type a-Si:H:F film was as good as ± 2.8%, and the photoelectric conversion efficiency showed the good value of 9.8%, and the characteristics were stable. Moreover, although the formed layer had a high conductivity, films with stable thickness and quality were obtained up to 1000 times film formation which was the maintenance cycle determined by particle generation.

[0073] <u>Example 4</u>

The microwave isolated plasma CVD apparatus shown in Fig.

4 (A) was used to form a selected Al film for a semiconductor element wiring was formed.

[0074]

A p-type single crystal silicon substrate (face orientation [100]; resistivity: 10 Ωcm) having a patterned BPSG film formed thereon was used as the substrate 412. First, after placing the silicon substrate 412 on the substrate support 413, evacuation of the inside of the plasma generating chamber 401 and the film forming chamber 411 was carried out through an evacuation system (not shown) to reduce the inside pressure to 10^{-6} Torr. Then, a heater (not shown) was energized to heat the silicon substrate 412 to 260°C and maintained the substrate at that temperature. Hydrogen gas at a flow rate of 200 sccm was introduced into the plasma generating chamber 411 via the plasma generating gas introducing opening 408. At the same time, dimethyl aluminium hydride (DMAlH) gas at a flow rate of 50 sccm was introduced into the film forming chamber 411 via the film forming gas introducing means 415. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the plasma generating chamber 401 at 0.1 Torr and the inside of the film forming chamber 411 at 0.03 Torr. A microwave power source of 2.45 GHz was used to supply a microwave power of 500 W through the annular waveguide 403 into the plasma generating chamber 401. Thus, a plasma was generated in the plasma generating chamber 401. At this time, the hydrogen gas introduced via the plasma generating gas introducing opening 408 was excited and decomposed in the plasma generating chamber 401 to form an active species, which was then transported toward the silicon substrate 412 to react with the dimethyl aluminium hydride gas introduced via the film forming gas introducing means 415, thereby forming an Al film in 0.8 μm thickness only on the silicon substrate

412. After the film was formed, the film formation speed, the uniformity and the resistivity were evaluated.

[0075]

It was confirmed that the film formation speed and the uniformity of the obtained Al film were as good as 80 nm/min and ± 2.7%, respectively and the film quality was as comparatively good as showing a resistivity of 4×10^{-6} Ωcm. Further, although the formed film was an electrically conductive film, films with stable thickness and quality were obtained up to 2000 times film formation which was the maintenance cycle determined by particle generation.

[0076] Example 5

The microwave isolated plasma CVD apparatus shown in Fig. 4 (A) was used to form a silicon oxide film for semiconductor element isolation.

[0077]

A p-type single crystal silicon substrate (face orientation [100]; resistivity: 10 Ωcm) was used as the substrate 412. First, after placing the silicon substrate 412 on the substrate support 413, evacuation of the inside of the plasma generating chamber 401 and the film forming chamber 411 was carried out through an evacuation system (not shown) to reduce the inside pressure to 10^{-6} Torr. Then, a heater (not shown) was energized to heat the silicon substrate 412 to 300°C and maintained the substrate at that temperature. Oxygen gas at a flow rate of 500 sccm was introduced into the plasma generating chamber 411 via the plasma generating gas introducing opening 408. At the same time, tetraetoxysilane (TEOS) gas at a flow rate of 200 sccm was introduced into the film forming chamber 411 via the film forming gas introducing means 415. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the plasma generating

chamber 401 at 0.1 Torr and the inside of the film forming chamber 411 at 0.05 Torr. A microwave power source of 2.45 GHz was used to supply a microwave power of 1500 W through the annular waveguide 403 into the plasma generating chamber 401. Thus, a plasma was generated in the plasma generating chamber 401. At this time, the oxygen gas introduced via the plasma generating gas introducing opening 408 was excited and decomposed in the plasma generating chamber 401 to form an active species, which was then transported toward the silicon substrate 412 to react with the tetraetoxysilane gas introduced via the film forming gas introducing means 415, thereby forming a silicon oxide film in 0.8 μm thickness on the silicon substrate 412. After the film was formed, the film formation speed, the uniformity, the dielectric strength, and the step coverage were evaluated. The step coverage was evaluated by observing a cross section of the silicon oxide film formed on Al steps formed in a line pattern of a line and space of 0.35 μm by a scanning electron microscope (SEM), and determining the ratio (covering factor) of the thickness of the film on the side surface of the step to the thickness of the film on the upper surface of the step.

[0078]

It was confirmed that the film formation speed and the uniformity of the obtained silicon oxide film were as good as 180 nm/min ± 2.7% and the film quality was as good as showing a dielectric strength 9.3 MV/cm and a covering factor 0.9. Further, films with stable thickness and quality were obtained up to 1000 times film formation which was the maintenance cycle determined by particle generation.

[0079] <u>Example 6</u>

The photo-assisted microwave plasma CVD apparatus is shown in Fig. 4 (A) was used to form a silicon oxide film for

semiconductor element gate isolation.

[0080]

A p-type single crystal silicon substrate (face orientation [100]; resistivity: 10 Ωcm) was used as the substrate 512. First, after placing the silicon substrate 512 on the substrate support 513, evacuation of the inside of the plasma generating chamber 501 and the film forming chamber 511 was carried out through an evacuation system (not shown) to reduce the inside pressure to 10^{-6} Torr. Then, an extra-high pressure mercury lamp of the illumination system 521 was turned on to irradiate the surface of the silicon substrate 512 with a light such that the illumination intensity at the surface of the silicon substrate 512 was 0.6 W/cm^2. Then, a heater (not shown) was energized to heat the silicon substrate 512 to 300°C and maintained the silicon substrate at that temperature. Oxygen gas at a flow rate of 500 sccm was introduced into the plasma generating chamber 501 via the plasma generating gas introducing opening 508. At the same time, monosilane gas at a flow rate of 50 sccm was introduced into the film forming chamber 511 via the film forming gas introducing means 515. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the plasma generating chamber 501 at 0.05 Torr and the inside of the film forming chamber 511 at 0.02 Torr. A microwave power source of 2.45 GHz was used to supply a microwave power of 500 W through the annular waveguide 503 into the plasma generating chamber 501. Thus, a plasma was generated in the plasma generating chamber 501. At this time, the oxygen gas introduced via the plasma generating gas introducing opening 508 was excited and decomposed in the plasma generating chamber 501 to form an active species such as oxygen atoms, which was then transported toward the silicon substrate 512 to react with the monosilane gas

introduced via the film forming gas introducing means 515, thereby forming a silicon oxide film in 0.1 μm thickness on the silicon substrate 512. After the film was formed, the film formation speed, the uniformity, the leak current, the dielectric strength, and the interface state density were evaluated. The interface state density was determined from a C-V curve under application of 1 MHz rf obtained by a capacity measuring device.

[0081]

It was confirmed that the film formation speed and the uniformity of the obtained silicon oxide film were as good as 110 nm/min ± 2.3% and the film quality was as very good as showing a leak current 4 x 10^{-11} A/cm^2, a dielectric strength 11 MV/cm and a interface state density 6 x 10^{10} cm^{-2}. Further, films with stable thickness and quality were obtained up to 1000 times film formation which was the maintenance cycle determined by particle generation.

[0082] Example 7

The biased microwave plasma CVD apparatus shown in Fig. 6 (A) was used to form a silicon oxide film and a silicon nitride film for reflection prevention for an optical element.

[0083]

A BK7 glass substrate was used as the substrate 612. After placing the glass substrate 612 on the substrate support 613, evacuation of the inside of the plasma generating chamber 601 and the film forming chamber 611 was carried out through an evacuation system (not shown) to reduce the inside pressure to 10^{-6} Torr. Then, a heater (not shown) was energized to heat the glass substrate 612 to 300°C and maintained the silicon substrate at that temperature. Nitrogen gas at a flow rate of 200 sccm was introduced into the plasma generating chamber 601 via the plasma generating gas introducing opening 608. At the same time, monosilane gas at a flow

rate of 30 sccm was introduced into the film forming chamber 611 via the film forming gas introducing means 615. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the forming chamber 611 at 10 mTorr. Then, a microwave power source of 2.45 GHz was used to supply a microwave power of 500 W through the annular waveguide 603 into the plasma generating chamber 601. Thus, a plasma was generated in the plasma generating chamber 601. At this time, the nitrogen gas introduced via the plasma generating gas introducing opening 608 was excited and decomposed in the plasma generating chamber 601 to form an active species such as nitrogen atoms, which was then transported toward the silicon substrate 612 to react with the monosilane gas introduced via the film forming gas introducing means 615, thereby forming a silicon nitride film in 61 nm thickness on the glass substrate 612.

[0084]

Next, oxygen gas at a flow rate of 200 sccm was introduced into the plasma generating chamber 601 via the plasma generating gas introducing opening 608. At the same time, monosilane gas at a flow rate of 30 sccm was introduced into the film forming chamber 611 via the film forming gas introducing means 615. Then, a conductance valve (not shown) provided in the evacuation system (not shown) was adjusted to maintain the inside of the forming chamber 611 at 10 mTorr. A microwave power source of 2.45 GHz was used to supply a microwave power of 500 W through the annular waveguide 603 into the plasma generating chamber 601. Thus, a plasma was generated in the plasma generating chamber 601. At this time, the oxygen gas introduced via the plasma generating gas introducing opening 608 was excited and decomposed in the plasma generating chamber 601 to form an active species such as oxygen atoms, which was then transported toward the

silicon substrate 612 to react with the monosilane gas introduced via the film forming gas introducing means 615, thereby forming a silicon oxide film in 86 nm thickness on the glass substrate 612. After the film was formed, the film formation speed and the reflective characteristics were evaluated.

[0085]

It was confirmed that the film formation speeds of the obtained silicon nitride film and silicon oxide film were as good as 110 nm/min, 130 nm/min, respectively, and as to the film quality, the optical characteristics were as very good as showing a reflectance 0.3% at about 500 nm. Further, films with stable thickness and quality were obtained up to 8000 times film formation which was the maintenance cycle determined by particle generation.

[0086]

[Effect of the Invention]

According to the present invention, a quartz tube for constituting the inner wall of the plasma generating chamber of a microwave CVD apparatus becomes unnecessary, and the problem that the introduction of microwaves into the plasma generating chamber is prevented by a thin film deposited on the inner wall of the quartz tube can be solved. Therefore, the maintenance cycle of the apparatus becomes long and the reliability and operating efficiency of the apparatus are improved.

[0087]

Furthermore, since the technique of evacuating the microwave waveguide 103 through the plasma generating chamber 101 and the slots 107, the inner pressure of the microwave waveguide becomes larger than that of the plasma generating chamber, so that no plasma is generated in the microwave waveguide and a plasma can be efficiently generated in the plasma generating chamber.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[Fig. 1] Schematic views showing an example of the microwave plasma CVD apparatus using an annular waveguide in accordance with the present invention;

[Fig. 2] Schematic views showing an example of the microwave plasma CVD apparatus using a disk-like waveguide in accordance with the present invention;

[Fig. 3] Schematic views showing an example of the microwave plasma CVD apparatus with a magnetic field in accordance with the present invention;

[Fig. 4] Schematic views showing an example of the microwave isolated plasma CVD apparatus in accordance with the present invention;

[Fig. 5] Schematic views showing an example of the photo-assisted microwave plasma CVD apparatus in accordance with the present invention;

[Fig. 6] Schematic views showing an example of the biased microwave plasma CVD apparatus in accordance with the present invention;

[Fig. 7] A schematic view showing an example of the microwave plasma CVD apparatus provided with an annular microwave introducing device and a disk-like microwave introducing device in combination in accordance with the present invention;

[Fig. 8] Schematic views showing an example of the microwave plasma CVD apparatus provided with an annular microwave introducing device and a disk-like microwave introducing device in combination in accordance with the present invention, wherein (B) shows the disk-like microwave introducing device and (C) shows the annular microwave introducing device;

[Fig. 9] Schematic views showing an example of the prior art microwave plasma CVD apparatus using a quartz tube